

Acentricity in the micas: an optical second harmonic study

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Abstract

Optical second harmonic analysis has been conducted on samples of muscovite, phlogopite, biotite, margarite, ephesite, lepidolite, and zinnwaldite. Ephesite, margarites, and zinnwaldites gave appreciable second harmonic signals, indicating that these minerals are non-centrosymmetric. These results provide the first physical evidence for the absence of a center of symmetry in the minerals and support published refinements of margarite and zinnwaldite. A very weak and questionable signal in a $2M_2$ lepidolite with a minor amount of admixed $1M$ lepidolite suggests that the $1M$ form may be acentric. The absence of optical second harmonics for the remaining samples is fairly convincing evidence that they are all centrosymmetric. These results are important in providing constraints on possible cation ordering schemes, and they illustrate the usefulness of second harmonic generation in detecting small deviations from centric symmetry which are difficult to observe by other techniques.

Introduction

Although the crystal structures of micas have been studied for many years, very few refined structures exist in which the absence of a symmetry center has been confirmed by physical tests. This is because Al-Si ordering has a minor effect on the statistical tests for centrosymmetry (Bailey, 1966), and because traditional tests for acentricity such as piezoelectricity are either not sensitive enough or require fairly large crystals. As a result, when refining the structures of micas, crystallographers commonly have employed the ideal centrosymmetric space-group symmetry (Bailey, 1974). Assuming an ideal space group imposes restrictions on the number of symmetry-independent tetrahedra and octahedra, precluding certain types of cation ordering. For example, $C2/m$ micas have only one symmetry-distinct tetrahedral site, and most common micas have only one independent interlayer cation site.

In a few cases successful refinements have been carried out in acentric subgroups of the ideal space group, the work of Guggenheim and Bailey (1975, 1977) being an excellent example. They showed that for margarite, $\text{CaAl}_2(\text{Al}_2\text{Si}_2)\text{O}_{10}(\text{OH})_2$, the space

group Cc instead of $C2/c$ gave an improved refinement and an ordered Al-Si distribution. An earlier study of margarite (Takéuchi, 1965), based on the centrosymmetric space group $C2/c$, gave a structure with a completely disordered arrangement of Al and Si, rather unusual for a structure having a 1:1 tetrahedral Al-Si ratio. Thus, knowledge of whether or not a crystal is centrosymmetric can sometimes be of crucial importance, but such information often is difficult to obtain.

Shortly after the discovery of lasers, Franken *et al.* (1961) found that optical harmonics were generated by noncentrosymmetric crystals when exposed to powerful laser beams. This effect, called Second Harmonic Generation (SHG), involves the emission of light from an acentric material at twice the frequency of the laser source.

Although SHG has been shown to be a highly reliable and sensitive physical test for acentricity, it is only beginning to be used as a tool for the structural characterization of minerals. Recent studies have applied SHG to fresnoite (Bechthold *et al.*, 1978), barylite (Robinson and Fang, 1977), and several clay minerals (Newnham *et al.*, 1977). In addition to being appreciably more sensitive than the piezoelect-

ric effect, the SHG test can be applied easily to both powders and single crystals, provided that acentric impurities such as quartz are not present. This paper presents SHG data collected on a number of micas to provide physical evidence for the absence of a center of symmetry in the minerals and to demonstrate the usefulness of the SHG experiment in detecting small deviations from centrosymmetric symmetry.

Experimental results

No complicated sample preparation is necessary for the SHG experiment, and all micas were examined in both powder and single-crystal form, using the apparatus illustrated in Figure 1. The instrument is similar to that used by Newnham *et al.* (1977), but the additional use of a signal integration technique has increased the sensitivity of the experiment over the previous limits. A neodymium glass laser provides coherent radiation at $1.06 \mu\text{m}$ containing 50–200 individual pulses in about 10^{-3} seconds. Optical filters block out unwanted background radiation, allowing only the fundamental wavelength to impinge upon the sample. Additional filters positioned in the exit beam transmit only the second harmonic to the photomultiplier. Signals from the two photodetectors are displayed on two oscilloscopes. A digital oscilloscope records the individual laser pulses from both the fundamental reference beam and the second harmonic. This allows comparison of pulse to pulse intensities as well as time synchronization between the second harmonic and the fundamental. The signals are integrated and displayed on a second oscilloscope to give quantitative data on the signal magnitudes.

Table 1 lists the results obtained from a number of mica samples. The margarites, zinnwaldites, and ephesite gave second harmonic intensities comparable to the signals obtained for kaolin minerals by Newnham *et al.* (1977). The Swedish lepidolite gave an extremely weak and questionable signal at least an order of magnitude above the noise level, and the remaining samples gave no signals down to the limits of detection.

The mica polytypes were identified using X-ray powder and single-crystal information. Since X-ray powder diffraction patterns of the $1M$ and $3T$ trioctahedral micas are virtually identical, zinnwaldites which gave signals raised the question whether the signal originated from the $3T$ acentric form or an acentric subgroup of the $1M$ form. A polarized laser beam experiment indicated that the electric vector in

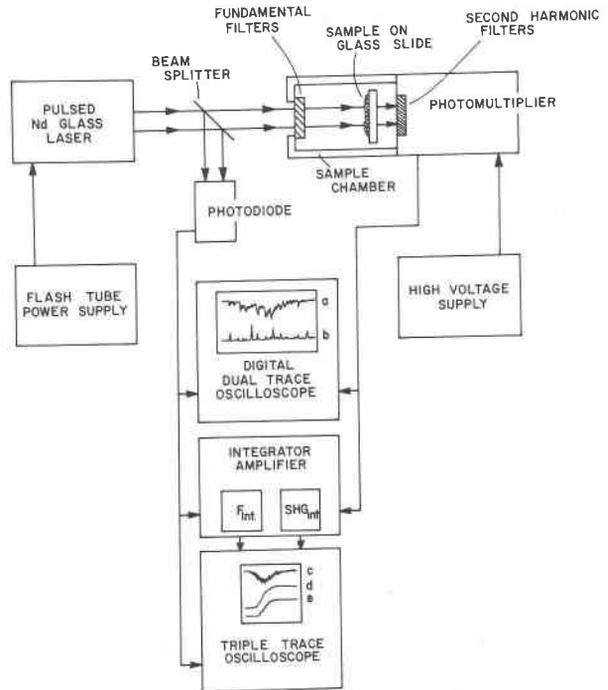


Fig. 1. Schematic diagram of the SHG instrument.

zinnwaldite lies within the (001) plane, whereas a $3T$ polytype must have its polarization direction perpendicular to (001) (Horsey, in preparation). Therefore, zinnwaldite is listed as a $1M$ polytype in Table 1. The Czechoslovakian lepidolite (sample B41 of Cerny *et al.*, 1970) was identified as the $2M_1$ polytype by Professor S. W. Bailey of the University of Wisconsin–Madison. The Swedish lepidolite is predominantly the $2M_2$ polytype, but powder diffraction patterns indicate the presence of a very minor amount of the $1M$ polytype.

Discussion and conclusions

The SHG results represent the first measurement of a physical property demonstrating that margarite, zinnwaldite, and ephesite are non-centrosymmetric, and support the choice of acentric space groups for margarite and zinnwaldite (Guggenheim and Bailey, 1975, 1977). The structure of ephesite has not yet been determined, but Smith and Yoder (1956) found that material from Postmasburg, South Africa, was predominantly the $2M_1$ polytype with indications of a minor amount of a $12M$ polytype. Schaller *et al.* (1967) reported that another sample from Postmasburg had the space group $C2/c$ or Cc . Our results and the similarity in compositions of ephesite, $\text{NaLiAl}_2(\text{Al}_2\text{Si}_2)\text{O}_{10}(\text{OH})_2$, and margarite,

Table 1. Results of the second harmonic analysis of selected micas

Mineral	Locality and Sample No.	Polytype	Signal
Muscovite	Chiquitos, Bolivia, #98713	$2M_1$	No
Muscovite	Methuen, Ontario, #112791	$2M_1$	No
Phlogopite	Edwards, New York, #96988	$1M$	No
Phlogopite	Lanark Co., Ontario, #90776	$1M$	No
Phlogopite	Llano, Texas, S. Bailey	$1M$	No
F-Phlogopite	Synthetic, R. Newnham	$1M$	No
Biotite	Bloomington, N. J., #112808	$1M$	No
Ephesite	Hotazel, S. Africa, #109218	$2M_1$	Yes
Margarite	Chester, Mass., #57122	$2M_1$	Yes
Margarite	Unionville, Pa., #89086	$2M_1$	Yes
Lepidolite	Varuträsk, Sweden, #92850	$2M_2 \gg 1M$	Yes(?)
Lepidolite	Biskupice, Czech., S. Bailey	$2M_1$	No
Zinnwaldite	Zinnwald, Germany, #99553	$1M$	Yes
Zinnwaldite	Zinnwald, Germany, #38912	$1M$	Yes

All numbered samples were obtained from the Harvard University Mineralogical Museum. Other samples were obtained from the designated sources.

$\text{CaAl}_2(\text{Al}_2\text{Si}_2)\text{O}_{10}(\text{OH})_2$, lead us to predict that ephesite has an ordered arrangement of tetrahedral Al and Si similar to that found in margarite. Based on the absence of tetrahedral Al–O–Al vibrations in the infrared spectrum, Farmer and Velde (1973) also have predicted an ordered distribution of tetrahedral Al and Si in ephesite. Substantial differences in size and charge for Li and Al make it likely that the octahedral cations also are ordered. An octahedral arrangement similar to that in margarite, with Li occupying the vacant M(1) site, is probable. Professor S. W. Bailey (personal communication, 1979) has found indications of a 6-layer triclinic structure for ephesite from Ephesus, and he has suggested that possibly we are seeing the effects of stacking symmetry.

The absence of optical harmonics for the remaining samples suggests (but does not prove conclusively, because signals may be below our limits of detection) that they are all centrosymmetric, in support of the published structure refinements. Most refinements of phlogopite were done in space group $C2/m$, although Steinfink (1962) initiated refinement in an acentric space group, only to find that the positional parameters shifted toward the centrosymmetric structure, and $C2/m$ was the space group finally assigned. The published refinements on lepidolites (Takeda and Burnham, 1969; Takeda *et al.*, 1971; Sartori *et al.*, 1973; Sartori, 1976, 1977) have all been carried out in centrosymmetric space groups. Guggenheim

and Bailey (1977) suggested that the octahedral ordering pattern observed in $C2$ zinnwaldites should be found in all F-rich zinnwaldites and lepidolites, but we find no convincing evidence from the SHG experiments that the $2M_1$ and $2M_2$ lepidolites which we examined are acentric. Dr. Stephen Guggenheim of the University of Illinois–Chicago Circle (personal communication, 1978) has reported that a structure refinement of a $2M_2$ lepidolite shows it to be centric while the $1M$ lepidolite is non-centrosymmetric. Admixture of a small amount of an acentric $1M$ polytype with the $2M_2$ Swedish lepidolite may account for the very weak and questionable SHG signal obtained for this sample. Although these results suggest that $1M$ lepidolite is acentric and $2M_2$ is centric, verification by SHG must await examination of a relatively pure $1M$ lepidolite.

The results for muscovite are particularly noteworthy and suggest that there is no ordering to an acentric subgroup. This agrees with Guggenheim and Bailey (1975), who found that the atomic coordinates of an acentric model converged to those of the centric disordered model. Ordering in $2M_1$ muscovite has been discussed in relation to the Al–Si disorder contribution to the configurational entropy (Ulbrich and Waldbaum, 1975; Robie *et al.*, 1976; Krupka *et al.*, 1979). Although $C2/c$ muscovite has two independent tetrahedra, all evidence indicates a disordered arrangement of Al and Si.

The SHG experiments confirm the ideal centrosymmetric space group for most micas. Our results also illustrate the usefulness of SHG in detecting small deviations from centric symmetry which are difficult to observe by other techniques, and they provide the first physical evidence for the absence of a symmetry center in margarite, zinnwaldite, and ephesite. Indirectly, our conclusions demonstrate the power and reliability of the subgroup refinement methods employed by Guggenheim and Bailey (1975, 1977).

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References

- Bailey, S. W. (1966) The status of clay mineral structures. *Clays Clay Minerals*, 14, 1–23.

- (1974) Cation ordering and pseudosymmetry in layer silicates. *Am. Mineral.*, 60, 175–187.
- Bechthold, P. S., S. Haussuhl, E. Michael, J. Eckstein, K. Recker and R. Wallrafen (1978) Second harmonic generation in fresnoite. *Phys. Lett. A.*, 65, 453–454.
- Černý, P., M. Rieder and P. Povondra (1970) Three polytypes of lepidolite from Czechoslovakia. *Lithos*, 3, 319–325.
- Farmer, V. C. and B. Velde (1973) Effects of structural order and disorder on the infrared spectra of brittle micas. *Mineral. Mag.*, 39, 282–288.
- Franken, P. A., A. E. Hill, C. W. Peters and G. Weinreich (1961) Generation of optical harmonics. *Phys. Rev. Lett.*, 7, 118–119.
- Guggenheim, S. and S. W. Bailey (1975) Refinement of the margarite structure in subgroup symmetry. *Am. Mineral.*, 60, 1023–1029.
- and ——— (1977) The refinement of zinnwaldite-1M in subgroup symmetry. *Am. Mineral.*, 62, 1158–1167.
- Krupka, K. M., R. A. Robie and B. S. Hemingway (1979) High-temperature heat capacities of corundum, periclase, anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$ glass, muscovite, pyrophyllite, KAlSi_3O_8 glass, grossular, and $\text{NaAlSi}_3\text{O}_8$ glass. *Am. Mineral.*, 64, 86–101.
- Newnham, R. E., J. J. Kramer, W. A. Shulze and G. W. Brindley (1977) Optical second harmonic signals from clay minerals. *Phys. Chem. Miner.*, 1, 379–384.
- Robie, R. A., B. W. Hemingway and W. H. Wilson (1976) Heat capacities of Calorimetry Conference copper and of muscovite $\text{KAl}_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$, pyrophyllite $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$, and illite $\text{K}_3(\text{Al}_7\text{Mg})(\text{Si}_{14}\text{Al}_2)\text{O}_{40}(\text{OH})_8$ between 15 and 375 K and their standard entropies at 298.15 K. *J. Res. U. S. Geol. Surv.*, 4, 631–644.
- Robinson, P. D. and J. H. Fang (1977) Barylite: its space group and crystal structure. *Am. Mineral.*, 62, 167–169.
- Sartori, F. (1976) The crystal structure of a 1M lepidolite. *Tschermaks Mineral. Petrogr. Mitt.*, 23, 65–75.
- (1977) The crystal structure of a $2M_1$ lepidolite. *Tschermaks Mineral. Petrogr. Mitt.*, 24, 23–37.
- , M. Franzini and S. Merlino (1973) Crystal structure of a $2M_2$ lepidolite. *Acta Crystallogr.*, B29, 573–578.
- Schaller, W. T., M. K. Carron and M. Fleischer (1967) Ephesite, a trioctahedral member of the margarite group, and related brittle micas. *Am. Mineral.*, 52, 1689–1697.
- Smith, J. V. and H. S. Yoder (1956) Experimental and theoretical studies of the mica polymorphs. *Mineral. Mag.*, 31, 209–235.
- Steinfink, H. (1962) Crystal structure of a trioctahedral mica: phlogopite. *Am. Mineral.*, 47, 886–896.
- Takeda, H. and C. W. Burnham (1969) Fluor-polyolithionite: a lithium mica with nearly hexagonal $(\text{Si}_2\text{O}_5)^{2-}$ ring. *Mineral. J. (Japan)*, 6, 102–109.
- , N. Haga and R. Sadanaga (1971) Structural investigation of polymorphic transition between $2M_2$, 1M-lepidolite, and $2M_1$ muscovite. *Mineral. J. (Japan)*, 6, 203–215.
- Takéuchi, Y. (1965) Structures of brittle micas. *Clays Clay Minerals*, 13, 1–25.
- Ulbrich, H. H. and D. R. Waldbaum (1975) Structural and other contributions to the third-law entropies of silicates. *Geochim. Cosmochim. Acta*, 40, 1–24.

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